In-Situ FTIR Kinetic Study in the Silylation of Low-k Films with Hexamethyldisilazane Dissolved in Supercritical CO₂

EDUARDO VYHMEISTER¹,², HÉCTOR VALDÉS-GONZÁLEZ³, LORENZO REYES-BOZO³, ROMAN RODRÍGUEZ-MAECKER¹, ANTHONY MUSCAT², L. ANTONIO ESTÉVEZ³, and DAVID SULEIMAN⁴

¹Departamento de Energía y Mecánica, Ingeniería Petroquímica, Calle Quijano y Ordoñez y Hermanas Páez, Universidad de las Fuerzas Armadas – ESPE extensión Latacunga, Cotopaxi-Latacunga, Ecuador
²Department of Chemical & Environmental Engineering, University of Arizona, Tucson, AZ, USA
³Universidad Central de Chile, Santiago, Chile
⁴Department of Chemical Engineering, University of Puerto Rico, Mayagüez

In-situ Fourier transform infrared spectroscopy measurements were obtained by using an innovative equipment to study the heterogeneous reaction between a hydrolyzed porous methylsilsesquioxane film and hexamethyldisilazane (HMDS) dissolved in CO₂ at supercritical conditions. Gas and solid infrared signatures were separated to obtain kinetic information of the heterogeneous reaction. A two-step reaction mechanism was observed: a first fast step controlled by kinetics and a second step controlled by the diffusion of the HMDS inside the porous material. Infrared information was used to derive a rate law expression of the silylation reaction between HMDS and Si-OH. A first order of reaction relative to the concentration of hydrophilic sites was observed with activation energy of 51.85 ± 1.25 kJ/mol.

Keywords: HMDS; Kinetics; Reaction engineering; Semiconductors; Silylation; Supercritical fluids

Introduction

The technological importance of silicon has driven an extensive body of research into the chemical functionalization of silicon surfaces. As feature size shrinks and nanotechnology remains an important focus of development, material interfaces become critical – the properties of a thin film with only a few nanometers thickness will be dominated by interface defects or interfacial layers (Rodriguez-Reyes and Teplyakov, 2007; Perrine and Teplyakov, 2010). The choice of surface modifying agent depends on the desired functional group for the intended application and the chemical state of the surface being modified. Ideally, functional groups would be incorporated within the synthesis steps, but physical–chemical conditions could establish the post-synthetic functionalization. Synthesis of porous materials, as mentioned by Athens et al. (2009), may require intermediate surface modification steps and/or pore size distribution modifications.

Functionalizing reagents, such as alkoxysilanes, chlorosilanes, and hexamethyldisilazane (HMDS), among others, are known by their tendency to react with hydroxyl groups. Surface treatments to modify the hydroxyl group concentration can be used if the synthesis process does not provide the adequate surface termination or adequate bonding sites for post-synthetic functionalization. Alkoxysilane, chlorosilanes, and HMDS can be delivered as a vapor, liquid solution, or dissolved in supercritical fluids (SCFs) (Vyhmeister et al., 2014; Combes et al., 1999; Cao et al., 2001; Chang et al., 2002; Himcinschi et al., 2002; Mor et al., 2002; Gorman et al., 2004; Xie and Muscat, 2004a, 2004b, 2005; Jones et al., 2004; Singh et al., 2006). Given the nanometric sizes involved in porous materials functionalization, SCF have shown to outclass the other methodologies due to their high diffusivity, absence of surface tension, and tunable solvating power.

HMDS has successfully been applied in silicon based surfaces modification and is less toxic than other silylating reagents, such as chlorosilanes. HMDS effectivly react with hydrophilic sites by the mechanism shown in Equations (1)–(3), where the s sub-index identifies a surface atom (Combes et al., 1999; Mor et al., 2002; Xie and Muscat, 2004b; Gun’ko et al., 2000).

\[
\begin{align*}
(CH_3)_3Si - NH &\rightleftharpoons (CH_3)_3Si - NH_2 + Si_s - O - Si(CH_3)_3 \\
(CH_3)_3Si - NH_2 + Si_s - O &\rightleftharpoons NH_3 + Si_s - O - Si(CH_3)_3
\end{align*}
\]